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Pesticide transport in an aerobic aquifer with variable pH—Modeling of a field scale injection experiment

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Abstract

Three-dimensional reactive transport simulations were undertaken to study the sorption and degradation dynamics of three herbicides in a shallow aerobic aquifer with spatially variable pH during a 216 days injection experiment. Sorption of two phenoxy acids [(±)-2-(4-chloro-2-methylphenoxy) propanoic acid] (MCPP) and [(±)-2-(2,4-dichlorophenoxy)propanoic acid] (dichlorprop) was found to be negligible. Degradation of the phenoxy acids was rapid after an initial lag phase. Degradation of the phenoxy acids could only be reproduced satisfactorily by growth-linked microbial degradation. The model fit to the field data was slightly improved if degradation was assumed to be influenced by the local pH that was observed to increase with depth (~4.5–5.7). In the observed pH-range the nitroaromatic herbicide [2-Methyl-4,6-dinitrophenol] (DNOC) was partly dissociated ($pK_a = 4.31$) and present in both the neutral and ionized form. The model simulations demonstrated that most of the observed spatial variation in sorption of DNOC could be explained by assuming that only the neutral form of DNOC was subject to sorption. A varying flow field was observed during the injection experiment and the model simulations documented that this most likely resulted in different migration paths for DNOC and the non-sorbing solutes. The model simulations indicated that degradation of DNOC was an important process. The degradation rate of DNOC remained constant over time and was simulated adequately by first-order kinetics. Again, the model fit to field observation was slightly improved if local pH was assumed to

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influence the degradation rate. Only the maximum utilization rate was estimated from the field data, while the remaining degradation parameters where successfully transferred from the laboratory study.

Keywords: Pesticides; Spatial variability; 3-D modeling; Field scale injection experiment

1. Introduction

Detailed knowledge of sorption and degradation processes is required when reliable estimates of herbicide persistence in groundwater systems are needed. Field data on herbicide transport are, however, often sparse and too limited to explore the sorption and degradation dynamics under natural conditions. Identifying reactive processes from field data is further complicated by the heterogeneity of natural groundwater systems, which makes it difficult to separate physical and reactive processes. The most common assumption made in field-scale simulations is that the parameters quantifying sorption and degradation are temporal and spatially invariant. While this assumption may be adequate for some applications, the reactive parameters often vary in time, e.g., by an increase in the degradation rate due to microbial growth, or, in space, due to e.g., geochemical heterogeneity in the aquifer.

Sorption of pesticides has been the focus of numerous laboratory but few field-scale experiments, see Wauchope et al. (2002) for a recent review. Variations in pH have, in general, only minor effects on sorption for pesticides with low polarity and low solubility. A large portion of modern pesticides are acidic or basic and are partially ionized within the normal range of soil pH. The partitioning coefficient (K_d) may be significantly different for the neutral and the dissociated form of the pesticide, whereby sorption becomes highly correlated to the soil pH. Natural variation in soil pH may therefore result in variable mobility of a pesticide at the field-scale (Nicholls and Evans, 1991; Moreau-Kervévan and Mouvet, 1998; Oliveira et al., 1999), and thereby affect biological degradation by varying the amount of bioavailable pesticide (Loux and Reese, 1992; Bresnahan et al., 2002).

First-order degradation kinetics are often assumed for field-scale pesticide simulations, which is argued applicable due to a low substrate concentration that do not support bacterial growth. A "low" concentration is, however, a loose and subjective definition. In laboratory batch experiments Toräng et al. (2003) found a shift in the biodegradation kinetics from first-order non growth to growth supporting degradation at concentrations as low as 1 μg/l and 10 μg/l for the phenoxy acids 2,4 -D and MCPP, respectively. These concentrations are within the range that may be expected from point sources (Gintautas et al., 1992). Growth-linked biodegradation may thus potentially occur in natural groundwater systems. Soil geochemistry, such as pH may influence the degradation rate as well. Variation in the degradation rate of the herbicide isoproturon in top soils was observed to be correlated to the soil pH by Walker et al., 2001 and Bending et al. (2003). In both studies degradation was found to increase when pH increased from ~6 to 7.5, and Bending et al. (2003) found that the degradation rate decreased again when pH was